

**PCT**WORLD INTELLECTUAL PROPERTY ORGANIZATION  
International Bureau

## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)–

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>C01B 25/04, 25/047</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 98/56712</b> <b>(43) International Publication Date:</b> 17 December 1998 (17.12.98)
<b>(21) International Application Number:</b> PCT/US98/11078 <b>(22) International Filing Date:</b> 1 June 1998 (01.06.98) <b>(30) Priority Data:</b> 08/871,037 9 June 1997 (09.06.97) US <b>(71) Applicant:</b> FMC CORPORATION [US/US]; 1735 Market Street, Philadelphia, PA 19103 (US). <b>(72) Inventors:</b> GUNKEL, Louis, T.; 51 Breece Drive, Yardley, PA 19067 (US). CROSBY, John; 8 Lumar Road, Lawrenceville, NJ 08648 (US). MUNDAY, Theodore, F.; 16 Steven Road, Kendall Park, NJ 08824 (US). BECK, Paul, J.; 13 Austin Road, Yardley, PA 19067 (US). <b>(74) Agent:</b> CALDWELL, John; Woodcock Washburn Kurtz Mackiewicz & Norris, 46th floor, One Liberty Place, Philadelphia, PA 19103 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>With amended claims and statement.</i>
<b>(54) Title:</b> A METHOD FOR EXTRACTING ANTIMONY FROM ELEMENTAL PHOSPHORUS		
<b>(57) Abstract</b>  A process for purifying elemental phosphorus that contains antimony using an oxidizer, such as hydrogen peroxide, peroxymonosulfate, peroxydisulfate, or a hypochlorite, in a two phase system containing water and phosphorus as the two liquids. A purified elemental phosphorus having 200 ppb or less antimony content.		

***FOR THE PURPOSES OF INFORMATION ONLY***

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

## A METHOD FOR EXTRACTING ANTIMONY FROM ELEMENTAL PHOSPHORUS

### Field of the Invention

This invention relates to the removal of a heavy metal from elemental phosphorus. More particularly, it concerns the production of an elemental phosphorus that contains a very low amount of antimony.

### Background of the Invention

Elemental phosphorus generally contains parts per million quantities of metals such as iron, arsenic, chromium, zinc, and antimony. The extent to which these metals are present in the phosphorus depends on the source of the phosphate ore that the phosphorus is extracted from and, to some extent, on the overall process used to produce and refine the elemental phosphorus. Of these metals, antimony has been most difficult to remove on an economical basis. Since a high antimony content can make the phosphorus unacceptable for use in certain food and electronics applications, it is important to develop a more economic method of removal.

This problem is perpetuated when elemental phosphorus is converted into phosphoric acid because the antimony in the phosphorus carries over into the phosphoric acid. Thus, in high value phosphoric acid products such as food grade acid and semiconductor grade acid, antimony can be a problem.

The problem is compounded by the fact that elemental phosphorus is not easy to work with. Because it spontaneously combusts when it is exposed to air, it is typically kept under a water blanket to prevent air contact. Because elemental phosphorus freezes at 44°C, it is typically kept at a higher temperature to keep the phosphorus fluid, so that it can be readily worked with, stored, and transported. To meet both these objectives, it is typically kept at a temperature above its melting temperature of 44°C to facilitate handling, and below the boiling temperature of water to preserve the water blanket. Thus, elemental phosphorus is usually handled as a two phase system, consisting of a phosphorus layer that is covered by a layer of water.

Hydrogen peroxide has been shown to remove iron in an elemental phosphorus system that consists of three phases: a water phase, a phosphorus phase and an organic phase that consists of an organo halide solvent, such as carbon tetrachloride or trichloroethylene. In that somewhat complicated system, the water, phosphorus and organic solvent were mixed and the phosphorus was dispersed in a larger volume of organo halide solvent to facilitate reaction between the hydrogen peroxide and the iron contained in the phosphorus. The art has been silent as to the use of that process in systems containing antimony or in simple phosphorus and water systems.

### **Summary**

Surprisingly, it has been discovered that elemental phosphorus can be purified by providing a two phase liquid, elemental phosphorus system, composed of liquid water and liquid phosphorus but no other liquid, which co-exist as an aqueous phase and an antimony containing phosphorus phase, dosing the system with an effective amount of an oxidizer selected from the group consisting of hydrogen peroxide, peroxydisulfate, peroxymonosulfate, Caro's acid or a salt thereof, sodium, potassium or calcium hypochlorite to lower the concentration of antimony in the phosphorus phase, and agitating the resultant mixture to effect separation of the antimony from the phosphorus phase.

In another aspect, it has been discovered the purified elemental phosphorus that is so produced contains less than 200 ppb antimony.

### **Detailed Description**

Elemental phosphorus has many allotropic forms. The phosphorus of this invention, commonly termed "elemental phosphorus" has a melting point of about 44.1°C and a boiling point of about 280.5°C. Such phosphorus is sometimes called white phosphorus in the text books because that is the color of the purified element. But, in the industry, it is commonly called yellow phosphorus, as that is, typically, the color of the industrially pure form.

Elemental phosphorus reacts spontaneously with air. Although phosphorus contact with air can be avoided by keeping the phosphorus in a vacuum or under

an inert gas blanket, air contact is typically avoided through the use of a water blanket. Because water is immiscible with, and less dense than phosphorus, it forms in a quiescent state a protective aqueous layer above the phosphorus that serves as an effective, economical interface that precludes phosphorus contact with  
5 air.

Antimony is intimately associated with the elemental phosphorus in the phosphorus phase. Although the exact manner in which antimony is bound to the phosphorus is unknown, it is connected in a manner that prevents the separation of the antimony and the phosphorus through mere water extraction or filtration.

10 Hydrogen peroxide is a water-soluble compound that is commercially available as an aqueous solution, typically of 5 wt % or 35 wt %. Because of its water solubility, the hydrogen peroxide added to the system tends to dissolve in the aqueous phase. As a consequence, the likelihood of a reaction occurring based on mere addition of the hydrogen peroxide to the aqueous phase is expected to be  
15 extremely low. It is further lowered by the fact that the antimony is present in extremely small amounts that are best measured and reported on a parts per million scale. Because of these factors, the likelihood of an effective contact between the hydrogen peroxide and the antimony containing phosphorus is, thus, extremely low, absent some other factor.

20 It has been determined that there are steps that can be taken to increase the likelihood of effective contact. One of these is to increase the level of agitation of the phosphorus system as much as possible to improve the degree of contact between the antimony and the hydrogen peroxide, while limiting the degree of agitation sufficiently to avoid having the phosphorus come in contact with, and  
25 reacting with, air.

As a rule, slow or poor mixing will prolong the time needed to remove the antimony. Optimum mixing as defined by safe engineering practices will decrease the time needed for the process to take effect and overly vigorous mixing will cause emulsions, sludge, and separation problems. Such mixing optimizes  
30 interfacial contact of the phosphorus and water phases to facilitate the purification process. Any device that generates sufficient agitation to mix the aqueous and phosphorus phases can be used: stirrers, mixers, a combination of baffles and

circulating pumps, or other agitating devices that do not create an undue risk of bringing the phosphorus into contact with air. Preferably, the aqueous hydrogen peroxide or other oxidizers are brought into intimate contact with the antimony containing phosphorus through judiciously vigorous mixing. The term "agitating" is used to connote an intermixing of the phases that occurs within these guidelines.

Other oxidizers, such as peroxydisulfate, peroxymonosulfate, hypochlorous acid or its salt sodium hypochlorite also perform well in the process of this invention and can be substituted for hydrogen peroxide in the process of this invention. Peroxydisulfate,  $S_2O_8$ , is available as the alkali, alkaline earth, and ammonium salt. Peroxymonosulfate,  $SO_5^{-2}$  is available in the acid form, as Caro's acid,  $H_2SO_5$ , and is also available under the DuPont trademark, Oxone in the form of the salt  $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$  that is available under the DuPont trademark Oxone trademark.

Increasing the hydrogen peroxide dosage also increases the effectiveness of the process by increasing the probability of contact of the hydrogen peroxide with the phosphorus phase. Although it is believed that the hydrogen peroxide reacts with antimony on a stoichiometric basis, it is generally desirable to have an excess of hydrogen peroxide relative to the antimony in order to facilitate the rate of the reaction. Thus, whether the reaction, in fact, is on a stoichiometric basis or not, the hydrogen peroxide is preferably used in excess.

Hydrogen peroxide works at any concentration; however, a concentration consistent with safe but reasonable productivity should be employed. Even at 0.1% hydrogen peroxide in the aqueous phase, significant reductions in antimony content of the phosphorus phase occur within a matter of hours. Although the peroxide concentration of the water phase is important, the number of moles of peroxide required to react with and remove a given number of moles of antimony in the phosphorus is also important, and either measure can be used to determine operating conditions and process results.

Because the hydrogen peroxide dosage required for the purification appears to be stoichiometric, a molar ratio of peroxide to antimony of at least one should be sufficient. But the very low (ppm range) concentration of antimony in

the phosphorus necessitates a large molar excess to effect separation in a reasonable amount of time. A hydrogen peroxide to antimony mole ratio of 300/1, as a practical matter can produce satisfactory results within several hours. The purification rate improves as the concentration of hydrogen peroxide in the treating aqueous phase goes up (i.e., the molar ratio of  $\text{H}_2\text{O}_2$  /Sb ratio goes up). The preferred molar ratios are a ratio of a least 1000:1 and a ratio within the range of 1000:1 to 3000:1 since these permit purification within three hours.

For practical reasons, an aqueous phase having 0.1 to 5 wt %  $\text{H}_2\text{O}_2$  can be used effectively, although 0.3 to 2% is preferred, and 0.5 to 1% is most preferred. High concentrations of peroxide can be used and if used would promote faster removal of the antimony. But for practical cost and safety reasons the preferred ranges have been provided herein. In a typical aqueous phase to phosphorus weight ratio of 4/1, a concentration of 0.5 percent hydrogen peroxide is sufficient to remove the antimony in about two hours. At this level, the mole ratio of  $\text{H}_2\text{O}_2$  to antimony in the phosphorus is about 2000 to 1. Concentrations higher than this at the same ratio of aqueous phase to total phosphorus do not improve the process by very much, at all. Of course the concentration of  $\text{H}_2\text{O}_2$  can be increased by simply reducing the amount of water in the aqueous phase of the system. In this manner the number of moles of  $\text{H}_2\text{O}_2$  used can be held to a constant or minimized, while the volume of the overall aqueous phase can be reduced. For safety and phosphorus recovery reasons, it is preferred to keep the concentration of the  $\text{H}_2\text{O}_2$  below five percent and preferably below 3.0 percent.

Controlling the temperature of the phosphorus system is critical during the purification process, since the purification cannot proceed efficiently with solid phosphorus. Thus, the temperature must be kept above  $44.1^\circ\text{C}$ , the melting temperature of phosphorus. Moreover, the boiling point of water must not be exceeded, where water is used as the air excluding barrier. Otherwise, the phosphorus can contact air. Given these constraints, a reasonable mixing temperature is within the range of from  $45\text{-}90^\circ\text{C}$  while operating at atmospheric pressure. However, the preferred operating range is  $50\text{-}70^\circ\text{C}$  and the most preferred range is  $50^\circ\text{-}60^\circ\text{C}$ . Of course, if a different air excluding barrier is used, then the preferred temperature ranges, although they may differ from those

provided herein, can be readily determined.

The length of time needed to remove the antimony from a portion of phosphorus is dependent upon the concentration of hydrogen peroxide in the water phase, the temperature of the system, and the degree of mixing that the phosphorus and the aqueous phase containing the hydrogen peroxide are subjected to. The  
5 better the mixing or contact between the phosphorus and the hydrogen peroxide in the aqueous phase, the quicker the process will work and cause the antimony to oxidize and transfer into the aqueous phase. Therefore, the best mixing consistent with good chemical engineering practices is recommended. The examples provided  
10 herein demonstrate that it is possible to reduce the antimony levels in elemental phosphorus from 40-50 ppm or higher to less than the detectable limits used in good laboratory practices (i.e. <0.1-0.2 ppm) by this process in a reasonable time period with proper mixing.

Using the above method, a significant reduction in antimony occurs.  
15 Reductions of at least 80, 95 or 98 percent are easily obtained. Typically, the reductions exceed 99.5%. The purified phosphorus typically contains <0.1-0.2 ppm antimony. This is the lower detectable limit for the graphite furnace/Atomic Absorption test used. Based on these results, the phosphorus purified according to the method can contain 200 ppb or less of antimony and can contain 100 ppb or  
20 less.

Notably, very little phosphorus is consumed in the process. Under the conditions described herein, typically recovery rates for the phosphorus are greater than 98%. Phosphorus recovery rates of at least 93% were obtained in all of the tests conducted. Generally rates lower than 98% were due to factors such as  
25 experimental error or not taking into account carryover into the aqueous phase.

Except for the oxidizer consumed during the purification process, very little oxidizer appears to be consumed by the process. Since, oxidizer usage during the process appears stoichiometric based on the analyses of the aqueous phase during the three hour extraction period, the peroxide solutions can be reused with only a  
30 small make up of peroxide being necessary until the build up of antimony in the aqueous phase becomes high enough to significantly affect the separation. By routine testing for antimony, schedules can be established for replenishing the water



used for the aqueous phase.

It is noteworthy that using dilute hydrogen peroxide to treat phosphorus, as described herein, always enhanced the appearance of the phosphorus. It lightened the color of the phosphorus and it provided a clearer product, presumably by reacting with insoluble organics that are present to a small extent in the phosphorus. Although these phenomena have not been quantified, these are values that are desired by phosphorus purchasers.

### EXAMPLES

10

#### **EXPERIMENTAL**

Durox™ Grade 35 percent hydrogen peroxide was used in the experiments. Durox is a trademark of FMC Corporation.

Two types of aqueous phases were studied in this work. One used deionized water and simply added the hydrogen peroxide to it to form the aqueous phase. The pH of this phase was usually 5-6 at the start of the test and then would quickly drop to ~ 2 as the hydrogen peroxide would react with a very small amount of the phosphorus to form some phosphoric acid. All of the initial scouting experiments were done using clean deionized water.

The other aqueous solution used was a sample of "phossy water." Phossy water is that water used in phosphorus production plants to cover phosphorus under storage, shipping, and transfer conditions. Because this water usually has phosphorus as well as other materials dissolved in it as a result of being in contact with phosphorus, it is segregated and reused in applications such as replacing phosphorus in rail cars when the phosphorus is pumped out at a user's facility.

There were no startling differences observed in going from one aqueous solution to the other as far as the process of removing antimony from phosphorus was concerned. The phossy water did have more impurities in it but those impurities did not hinder the removal of antimony. The hydrogen peroxide was less stable in the phossy water than it was in the de-ionized water but it was stable enough over an eight hour period to accomplish the extraction process. The phossy water containing ~2.6 % hydrogen peroxide was tested with and without 316

stainless steel coupons present in the liquid and vapor spaces and there was no difference in peroxide stability due to the presence of the stainless steel.

All of the experiments carried out in this work except No. 8 were conducted in the apparatus described below:

5        See through components were chosen, so that the extraction process could be viewed. A Plexiglas water bath 18 inches long by 13 inches wide and 7 inches deep was set in a larger stainless steel tray in a fume hood. A glass beaker was used as the vessel for the extraction to take place in. This beaker was a 300 milliliter capacity Pyrex Model 1060 whose inside measurement was 60 mm, (2.36  
10   inches) wide in diameter and 11.40 mm deep, (4.5 inches).

An isothermal immersion circulator supplied circulation and heat to the water in the bath. A 316 SS propeller type stirrer on a 1/4 inch stainless steel shaft was used for mixing the water and the phosphorus. The propeller had three blades, each blade was ~ 1/2 inch in diameter, with an overall stirrer radius of ~ 1.5  
15   inches. The stirrer speed used for most of the tests was 300 RPM.

### **Example No. 1**

Using the apparatus described above, 100 milliliters of water were charged  
20   to a beaker and heated to 60°C. Forty-three and one tenth grams of elemental phosphorus (P4) were then added to the water in the beaker. The P4 melted and fell to the bottom of the beaker. The stirrer was then started at 300 RPM and 40 grams of 10.9 % hydrogen peroxygen solution were added to the water phase of the mixture (H<sub>2</sub>O<sub>2</sub> final strength ~ 3.1 % in aqueous phase in the beaker). The  
25   mixture was stirred for three hours at temperature and then the phosphorus was sampled with a syringe and analyzed.

#### Antimony

	P4 Analysis initially	47 PPM
30	P4 Analysis after 3 hours	<0.2 PPM

**Example No. 2**

Using the apparatus described above, 100 milliliters of water were charged to a beaker and heated to 60°C. Forty and one half grams of elemental P4 were then added to the beaker containing the water. The P4 melted and fell to the bottom of the beaker. The stirrer was then started at 300 RPM and 40 grams of 10.9 % hydrogen peroxygen solution were added to the water phase of the mixture (H<sub>2</sub>O<sub>2</sub> final strength ~ 3.1 % in aqueous phase in the beaker). The mixture was stirred for three hours at temperature and then the phosphorus was sampled with a syringe and analyzed.

**Antimony**

Sb Analysis Initially

47 PPM

Sb after 3 hours

&lt;0.1 PPM

**Example No. 3**

The apparatus described above was charged with the following:

146.0 grams of water  
34.75 grams of phosphorus  
20.59 grams of an aqueous H<sub>2</sub>O<sub>2</sub> solution of 10.9 percent concentration

Procedure: The water was added to a beaker and the beaker was then placed in the 60°C bath. The phosphorus was then added and allowed to melt then the stirrer was inserted and started at 300 rpm. The hydrogen peroxide was then added to the mix and the test was started.

## Run Data

	<u>Time</u>	<u>pH</u>	<u>% H<sub>2</sub>O<sub>2</sub></u>
	0 min	6.0	1.47
5	60 min	5.0	1.48
	120 min	5.0	
	170 min	4.0	1.50

The run was stopped after three hours. The beaker containing the P4 was removed from the bath and cooled in an ice bath. The treated phosphorus and aqueous phases were separated and weighed. The recovered phosphorus weighed 33.72 grams (97.1 % recovery) and the aqueous layer weighed 132.44 grams.

The analysis of the two samples showed less than 0.1 ppm antimony in the phosphorus after treatment.

<u>Analysis (ppm)</u>	<u>Initial P4</u>	<u>Final P4</u>	<u>Aqueous Phase</u>
Antimony	42 ppm	<0.1 ppm	9.2 ppm
Phosphorus			3200 ppm

At test completion, 99.7 percent of the antimony had been removed from the elemental phosphorus and transferred into the aqueous phase. Based on the level of phosphorus in the aqueous phase, the amount of phosphorus lost was 1.2 percent or phosphorus yield was 98.8 percent. The treated phosphorus was clear and white.

**Example No. 4**

The apparatus described above was charged with the following:

150.01	grams of water
30.66	grams of phosphorus
5.00	grams of an aqueous H <sub>2</sub> O <sub>2</sub> solution of 35% concentration

Procedure: H<sub>2</sub>O<sub>2</sub> was added to a beaker that contained the water, and then the

beaker was placed in a 60°C bath. The phosphorus was then added and allowed to melt before the stirrer was inserted and started at 300 rpm. The mixture was stirred for three hours. The following data were recorded.

## 5 Run Data

	<u>Time</u>	<u>pH</u>	<u>% H<sub>2</sub>O<sub>2</sub></u>
	0 min	6.0	1.26
	60 min	5.5	1.24
10	120 min	5.0	1.27
	180 min	3.5	1.22

The run was stopped after three hours. The beaker containing the P<sub>4</sub> was removed from the bath and cooled in an ice bath. The treated phosphorus was separated from the aqueous phase and weighed. The recovered phosphorus weighed 30.20 grams (98.5 % recovery).

The analysis of the sample showed less than 0.2 ppm antimony in the phosphorus after treatment.

	<u>Analysis (ppm)</u>	<u>Initial P<sub>4</sub></u>	<u>Final P<sub>4</sub></u>	<u>Aqueous Phase</u>
20	Antimony	42 ppm	<0.2 ppm	12 ppm
	Phosphorus			3900 ppm

At test completion, 99.3 percent of the antimony had been removed from the elemental phosphorus and transferred into the aqueous phase. Based on the level of phosphorus in the aqueous phase, the amount of phosphorus lost was 1.4 percent or phosphorus yield was 98.6 percent. The treated phosphorus was clear and white.

## 30 Example No. 5

The apparatus described above was charged with the following:

- 150.0 grams of water,
- 31.91 grams of phosphorus
- 14.95 grams of an aqueous H<sub>2</sub>O<sub>2</sub> solution of 10.9 % concentration

Procedure: The water was added to a beaker and the beaker was then placed in the 60°C bath. The phosphorus was added and allowed to melt before the stirrer was inserted and started at 300 rpm. The hydrogen peroxide was then added to the mix and the test was started.

#### Run Data

	<u>Time</u>	<u>pH</u>	<u>% H<sub>2</sub>O<sub>2</sub></u>
10	0 min		1.10
	60 min	5.5	1.06
	120 min	5.0	1.12
	180 min	4.0	1.21

The run was stopped after three hours. The beaker containing the P4 was removed from the bath and cooled in an ice bath. The treated phosphorus was separated from the aqueous phase and weighed. The recovered phosphorus weighed 31.37 grams (98.3 % recovery), and the aqueous layer weighed 118.66 grams.

Analysis showed less than 0.2 ppm antimony in the phosphorus after treatment.

	<u>Analysis (ppm)</u>	<u>Initial P4</u>	<u>Final P4</u>	<u>Aqueous Phase</u>
25	Antimony	42 ppm	<0.2 ppm	12 ppm
	Phosphorus			3600 ppm

At test completion, 99.3 percent of the antimony had been removed from the elemental phosphorus and transferred into the aqueous phase. Based on the level of phosphorus in the aqueous phase, the amount of phosphorus lost was 1.3 percent or phosphorus yield was 98.7 percent. The treated phosphorus was clear and white.

**Example No. 6**

The apparatus described above was charged with the following:

5	150.93	grams of water
	29.60	grams of phosphorus
	7.44	grams of an aqueous H <sub>2</sub> O <sub>2</sub> solution of 10.9 % concentration

10    Procedure:    The water was added to a beaker and the beaker was then placed in the 60°C bath. The phosphorus was added to the beaker and allowed to melt before the stirrer was inserted and started at 300 rpm. The hydrogen peroxide was then added to the mix and the test was started.

15    Run Data

	<u>Time</u>	<u>pH</u>	<u>% H<sub>2</sub>O<sub>2</sub></u>
	0 min	6.0	0.58
	60 min	6.0	0.54
20	120 min		0.54
	170 min	4.0	0.52

The run was stopped after three hours. The beaker containing the P4 was removed from the bath and cooled in an ice bath. The treated phosphorus and aqueous phase were separated and weighed. The recovered phosphorus weighed  
25    29.61 grams (100 % recovery).

The analysis of the sample showed less than 0.2 ppm antimony in the phosphorus after treatment.

	<u>Analysis (ppm)</u>	<u>Initial Sb</u>	<u>Final Sb</u>
30	Antimony	42	<0.2 ppm

P4 recovery = 100 %

At test completion, 99.3% of the antimony had been removed and the elemental phosphorus solution appeared clear.

**Example No. 7**

5

The apparatus described above was charged with the following:

	100	grams of water
	26.28	grams of phosphorus
10	1.0	grams of an aqueous H <sub>2</sub> O <sub>2</sub> of 10.9 % concentration

Procedure: The water was added to beaker, which was then placed in a 60°C bath. The phosphorus was added and allowed to melt before the stirrer was inserted and started at 300 rpm. One gram of H<sub>2</sub>O<sub>2</sub> was then added and the test

15

**Run Data**

	<u>Time</u>	<u>% H<sub>2</sub>O<sub>2</sub></u>
20	0 min	0.10
	40 min	
	120 min	

The run was stopped after two hours. The beaker containing the P<sub>4</sub> was removed from the bath and cooled in an ice bath. The P<sub>4</sub> was removed and weighed and analyzed.

	24.48 grams P <sub>4</sub> recovered		
	107.40 grams of aqueous phase recovered		
30	<u>Analysis (ppm)</u>	<u>In Starting P<sub>4</sub></u>	<u>In Final P<sub>4</sub></u> <u>In Aqueous Phase</u>
	Antimony	42 ppm	6.5 ppm    11.0 ppm
	Phosphorus		0.04%



Percent Sb removed from P4 = 91% Percent Sb found in Aqueous Phase = 89.9%  
P4 recovery based on P4 in Aqueous Phase = 99.84%

At test completion, 84.5% of the antimony had been removed and the  
5 elemental phosphorus solution appeared clear. This test demonstrates that even low  
amounts of hydrogen peroxide remove antimony.

**Experiment No. E9955-60 (Experiment No. 8)**

10 A two liter fluted resin kettle. equipped with efficient stirring and a  
nitrogen padding system to keep air from the reactor, was charged with the  
following:

Charge:	500.00	grams of water
15	350.00	grams of phosphorus
	16.00	grams of an H <sub>2</sub> O <sub>2</sub> solution of 35 % concentration

Procedure: The water was added to the two liter resin flask. The flask was  
then placed in a 60°C bath. The phosphorus was added and allowed to melt before  
20 the stirrer was inserted and started at 600 rpm. The hydrogen peroxide was then  
added to the mix and the test was started. The phosphorus phase was sampled  
during the test at 15, 45 and 105 minute intervals to check the degree of antimony  
extraction over time. The results are tabulated below.

25 Run Data

	<u>Time</u>	<u>% H<sub>2</sub>O<sub>2</sub></u>	<u>PPM Antimony in P4</u>
	0 min	1.08 %	42
	15 min	1.09 %	9.7
30	45 min	0.97 %	0.66
	105 min	0.80 %	<0.2

The run was stopped after 105 minutes when the antimony level in the

phosphorus dropped to <0.2 ppm.

### Experiment 9

- 5           Using the procedure of Example 1, the following oxidizing agents were tested for their efficacy in treating elemental phosphorus. The charges were added to a 300 ml beaker and stirred at 60°C for several hours, after which the phosphorus and aqueous phases were separated and analyzed.

10		$\text{Na}_2\text{S}_2\text{O}_8$	$\text{SO}_5^{-2*}$	$\text{NaOCl}$
	P4 Charge	30 grams	30 grams	29.6 grams
	Water	150 grams	150 grams	(with hypochlorite)
	Oxidant	20 grams	54 grams	250 grams
15	Sb (original)	40 ppm	40 ppm	40 ppm
	Sb (final)	13 ppm	<0.1 ppm	<0.1 ppm

20   \* As  $2\text{KHSO}_5\text{KHSO}_4\text{K}_2\text{SO}_4$  (Oxone®peroxymonosulfate)

We claim:

1. A process for purifying elemental phosphorus that contains antimony, comprising the steps of providing a two phase, liquid elemental phosphorus system, composed of liquid water and liquid phosphorus but no other liquid, which co-exist as an aqueous phase and an antimony containing phosphorus phase, dosing the system with an effective amount of an oxidizer such as hydrogen peroxide, a peroxydisulfate, a peroxymonosulfate, or a hypochlorite, and agitating the resultant mixture to lower the concentration of antimony in the phosphorus phase and to effect a separation of antimony from the phosphorus.
2. The process of claim 1, wherein the oxidizer is dosed in a molar ratio of oxidizer to antimony of at least 1 to 1 and wherein the agitating mixture occurs at a temperature above the melting point of phosphorus, but below the boiling point of water.
3. The process of claim 2, wherein the ratio is at least 300 to 1, the temperature of the phosphorus is maintained within the range of from 50 to 70°C, and the mixture is agitated for a period of at least one hour.
4. The process of claim 2, wherein the ratio is within the range of from 1000 to 1 to 3000 to 1 and the temperature of the phosphorus is maintained within the range of 50 to 70°C for a period of time sufficient for the antimony content to be reduced by at least 80%.
5. The process of claim 4, wherein the antimony content of the phosphorus phase is reduced by at least 95 %.
6. The process of claim 4, wherein the antimony content of the phosphorus phase is reduced by at least 99%.
7. The process of claim 3, wherein the water phase is separated from the phosphorus, and used as a peroxide source for continuing the process with a new batch of phosphorus.
8. The process of claim 2, wherein the oxidizer is hydrogen peroxide.
9. The process of claim 3, wherein the oxidizer is hydrogen peroxide.
10. The process of claim 4, wherein the oxidizer is hydrogen peroxide.

11. The purified phosphorus product made according to the process of claim  
3.

12. The purified phosphorus product made according to the process of claim  
4.

5 13. The purified phosphorus product made according to the process of claim  
5.

14. The purified phosphorus product made according to the process of claim  
6.

10 15. An elemental phosphorus for use in applications requiring very low levels  
of antimony as an impurity in the phosphorus, comprising the phosphorus made  
according to the process of claim 5.

16. An elemental phosphorus for use in applications requiring very low levels  
of antimony as an impurity in the phosphorus, comprising the phosphorus made  
according to the process of claim 6.

15 17. A process for purifying elemental phosphorus, comprising dosing a two  
phase elemental phosphorus system, having an aqueous phase and an immiscible  
liquid elemental phosphorus phase containing antimony, with an effective amount  
of hydrogen peroxide to lower the concentration of antimony in the phosphorus and  
to improve the clarity and lighten the color of the phosphorus, agitating the  
20 resultant mixture at a temperature above the melting point of phosphorus, but  
below the boiling point of water, and then separating the aqueous and phosphorus  
phases to recover a phosphorus lower in antimony content.

**AMENDED CLAIMS**

[received by the International Bureau on 16 November 1998 (16.11.98);  
original claims 1-10 and 15-16 amended; remaining claims unchanged  
(2 pages)]

1. A process for purifying elemental phosphorus that contains antimony, comprising the steps of providing a two phase, liquid elemental phosphorus system, composed of liquid water and liquid phosphorus but no other liquid, which co-exist as an aqueous phase and an antimony containing phosphorus phase, dosing the system with an effective amount of an oxidizer selected from the group consisting of hydrogen peroxide, a peroxydisulfate, a peroxymonosulfate, and a hypochlorite, and agitating the resultant mixture to lower the concentration of antimony in the phosphorus phase and to effect a separation of antimony from the phosphorus.
2. The process of claim 1 wherein the oxidizer is dosed in a molar ratio of oxidizer to antimony of at least 1 to 1 and wherein the agitating mixture occurs at a temperature above the melting point of phosphorus, but below the boiling point of water.
3. The process of claim 2 wherein the ratio is at least 300 to 1, the temperature of the phosphorus is maintained within the range of from 50 to 70°C, and the mixture is agitated for a period of at least one hour.
4. The process of claim 2 wherein the ratio is within the range of from 1000 to 1 to 3000 to 1 and the temperature of the phosphorus is maintained within the range of 50 to 70°C for a period of time sufficient for the antimony content to be reduced by at least 80%.
5. The process of claim 4 wherein the antimony content of the phosphorus phase is reduced by at least 95 %.
6. The process of claim 4 wherein the antimony content of the phosphorus phase is reduced by at least 99%.
7. The process of claim 3 wherein the water phase is separated from the phosphorus, and used as a peroxide source for continuing the process with a new batch of phosphorus.
8. The process of claim 2 wherein the oxidizer is hydrogen peroxide.
9. The process of claim 3 wherein the oxidizer is hydrogen peroxide.
10. The process of claim 4 wherein the oxidizer is hydrogen peroxide.
11. The purified phosphorus product made according to the process of claim 3.
12. The purified phosphorus product made according to the process of claim 4.

13. The purified phosphorus product made according to the process of claim 5.

14. The purified phosphorus product made according to the process of claim 6.

5 15. An elemental phosphorus for use in applications requiring very low levels of antimony as an impurity in the phosphorus, comprising the phosphorus made according to the process of claim 5 and contains 0.2 or fewer ppm antimony.

10 16. An elemental phosphorus for use in applications requiring very low levels of antimony as an impurity in the phosphorus comprising the phosphorus made according to the process of claim 6 and contains less than 0.1 ppm antimony.

15 17. A process for purifying elemental phosphorus, comprising dosing a two phase elemental phosphorus system, having an aqueous phase and an immiscible liquid elemental phosphorus phase containing antimony, with an effective amount of hydrogen peroxide to lower the concentration of antimony in the phosphorus and to improve the clarity and lighten the color of the phosphorus, agitating the resultant mixture at a temperature above the melting point of phosphorus, but below the boiling point of water, and then separating the aqueous and phosphorus phases to recover a phosphorus lower in antimony content.

STATEMENT UNDER ARTICLE 19

Claim 1 has been amended to replace "such as" with classic Markush language of "selected from the group consisting of" and claims 15 and 16 have been amended to reflect specific levels of antimony. Support for these amendments are found throughout the specification, for example, at page 2, lines 14-16 and page 5, lines 29-34 and the examples in the specification. The other claims have been amended to correct punctuation.

No new matter has been added.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 98/11078

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B25/04 C01B25/047

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 8307 Derwent Publications Ltd., London, GB; Class E36, AN 83-17035K XP002076553 &amp; SU 919 989 B (KAZA PHOSPHOR IND) see abstract</p> <p style="text-align: center;">---</p>	1, 17
A	<p>DATABASE WPI Section Ch, Week 8121 Derwent Publications Ltd., London, GB; Class E36, AN 81-37819D XP002076554 &amp; SU 763 261 B (LENGD BASIC CHEM) see abstract</p> <p style="text-align: center;">---</p>	1, 17
P, A	<p>WO 97 28086 A (FMC CORP) 7 August 1997 see the whole document</p> <p style="text-align: center;">-----</p>	1, 17

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance  
 "E" earlier document but published on or after the international filing date  
 "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)  
 "O" document referring to an oral disclosure, use, exhibition or other means  
 "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
 "&" document member of the same patent family

Date of the actual completion of the international search

4 September 1998

Date of mailing of the international search report

21/09/1998

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Rigondaud, B



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 98/11078

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9728086 A	07-08-1997	US 5670126 A AU 2258297 A	23-09-1997 22-08-1997
-----			